Fuel 139 (2015) 652–658

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

# Re-addition of antioxidant to aged MEROX and hydroprocessed jet fuels

Paul M. Rawson [a,c,*], Christy-Anne Stansfield [a], Renée L. Webster [a,b], David Evans [a]

[a] Defence Science and Technology Organisation, 506 Lorimer St, Fishermans Bend, Victoria 3207, Australia
[b] Australian Centre for Research on Separation Science, School of Chemistry, Monash University, Wellington Rd, Clayton, Victoria 3800, Australia
[c] School of Aerospace, Mechanical and Manufacturing Engineering, RMIT University, 124a Latrobe Street, Melbourne, Victoria, Australia

## HIGHLIGHTS

- Effect of re-addition of antioxidant to aged and processed fuels.
- Addition of antioxidant to hydroprocessed fuel past mandated time.
- Antioxidant depletion rates for aged fuels.
- Influence of readdition of antioxidant on induction times.

## ARTICLE INFO

*Article history:*
Received 9 May 2014
Received in revised form 7 July 2014
Accepted 11 September 2014
Available online 24 September 2014

*Keywords:*
Antioxidant
Jet fuel
MEROX
Hydrotreatment

## ABSTRACT

Long term storage of aviation turbine fuels often requires the use of antioxidants with many military fuel specifications mandating its addition for hydroprocessed fuels. This work examines the influence of antioxidants on aged and freshly refined aviation turbine fuels of various types, some containing antioxidant at manufacture and others not. The rate of antioxidant depletion is reported along with the re-stabilised fuel's oxidation induction periods. It was found that some fuel types do not benefit from re-addition of antioxidant and no improvement was observed for inhibition of hydroperoxide formation in aged fuels, however oxidation induction times were improved for re-addition of antioxidant for all fuels examined. A simple method for assessing the degree of hydroprocessing of an unknown fuel was also examined with limited success.

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## 1. Introduction

Storage stability is a significant concern for long term and strategic storage of jet fuels. Storage stability is defined as a fuel's resistance to peroxide and sediment formation. Other measures of stability also exist and include oxygen induction times. Jet fuels are manufactured by various processing methods including straight run, MEROX and hydroprocessing [1]. Different fuel refinery processing methods are known to affect the storage stability of fuels. Some fuels are known to have poor storage stability based on their processing such as hydroprocessed fuels which are generally considered to be fast oxidisers [2,3]. Hydroprocessing will remove naturally occurring antioxidants including oxygen, sulfur and nitrogen heteroatoms [4]. Unstabilised fuels will tend to react with oxygen to form hydroperoxides which will affect aircraft fuel system seals, diaphragms and materials made of neoprene, nitrile rubber and Buna-N [5–9]. Rates of formation and decomposition of peroxides are driven by storage temperatures, duration and the availability of oxygen [10,11]. Peroxides once formed in a fuel, will initiate autoxidation reactions ultimately forming sediments and gums which lead to increased maintenance, poor performance and engine failures [3,12,13].

To ensure satisfactory storage stability and inhibit peroxide formation, some military and civil fuel specifications require the addition of antioxidant to hydroprocessed fuels immediately after processing and before the fuel is exposed to the atmosphere [14,15]. This is done with the purpose of preventing gum formation and peroxidation after manufacture [16]. Previous studies have shown that hydroprocessed fuels will exhibit peroxide formation rates 200 times greater than a non hydrotreated fuel [9]. Once all available antioxidants are depleted the rate of formation is so rapid that for the antioxidant to be effective it should be added at the time of processing.

Synthetic phenolic antioxidants have routinely been used to stabilise fuels by preventing peroxide build up [17–19]. Synthetic phenolics act to disrupt the chain of peroxidation reactions by

* Corresponding author at: Defence Science and Technology Organisation, 506 Lorimer St, Fishermans Bend, Victoria 3207, Australia.
*E-mail address:* Paul.Rawson@dsto.defence.gov.au (P.M. Rawson).

http://dx.doi.org/10.1016/j.fuel.2014.09.048
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**Table 1**
Ambient aged fuels peroxide concentrations pre and post addition of antioxidant and measured after 26 weeks aging at 43 °C. *Note* PV = peroxide value.

| Sample name | Fuel type | Finishing process | Years in ambient storage | PV initial | PV 26 weeks at 43 °C with 25 ppm antioxidant added (ppm) | Initial antioxidant present (ppm) |
|---|---|---|---|---|---|---|
| Aging 7 | F-34 | MEROX blend | 0.5 | 0.0 | 0.0 | 0.0 |
| Aging 6 | F-34 | MEROX blend | 3 | 0.0 | 7.2 | 0.0 |
| Aging 5 | F-34 | MEROX Blend | 10 | 0.5 | 8.5 | 0.0 |
| Aging 4 | F-34 | MEROX blend | 11 | 0.0 | 6.4 | 0.0 |
| Aging 3 | F-34 | MEROX blend | 12 | 0.0 | 7.4 | 8.1 |
| Aging 2 | F-34 | MEROX Blend | 17 | 0.0 | 7.3 | 9.4 |
| Aging 1 | Jet A1 | MEROX blend | 17 | 0.0 | 3.4 | 0.0 |

forming a stable radical but are not known to be effective in inhibiting those peroxides already in the fuel [20].

Work by Love et al. [7] on fuel related problems in gas turbine engines summarised the effect of peroxide formation finding the following;

- "Fuels that contained peroxide that attacked rubbers showed little or no improvement following addition of antioxidant, as the useful properties of the additive were quickly absorbed without a reduction in peroxide content.
- Little improvement was achieved when all traces of existing peroxides were removed from the fuel by chemical treatment as they quickly reform.
- Removal of existent peroxides from the fuel, followed by immediate addition of an antioxidant inhibited peroxide reformation.
- Blending of fast oxidising fuels with non-hydroprocessed fuels improved resistance to peroxide formation."

Normally once a jet fuel has been stabilised with antioxidant it has no further requirement for re-addition under normal storage conditions. Fuels in storage have no defined in-service deterioration limits with respect to peroxide formation, but the deterioration may be monitored via other properties such as existent gum formation. Currently for some fuels in long term storage there is no limit placed on life as long as those fuels pass periodic recertification testing.

Fuel samples of uncertain provenance may be mixtures of fuels produced by varied finishing processes. Currently there is no simple method for determining the level of an unknown fuel's hydrotreatment, or the degree of hydroprocessed component of a mixture. A simple method to establish unknown fuels level of hydrotreatment based on the conversion of naphthalene to tetralin and decalin as a guide was examined.

This work explores the potential for re-addition of antioxidant to aged hydroprocessed fuels and to a hydroprocessed fuel that did not have antioxidant added during production. These hydroprocessed fuels are compared with a range of straight run and MEROX fuels of various ages.

## 2. Experimental

### 2.1. Samples

Three different fuel types were examined plus a 'model fuel' assessed as a possible reference fuel. Fuel samples used in the experiment were either Jet A-1, F-34 (Jet A-1 plus military additive package) or F-44 (military aviation fuel for use on ships with additive package). The F-34 and F-44 all met the DEF(AUST) 5240D aviation turbine fuel specification [16] and all had the fuel system icing inhibitor (FSII), static dissipater additive and corrosion inhibitor additive package. All samples were taken either directly from the refinery or from air base tankage where the fuel was supplied to the base consistently from a single refinery. All were stored in 1 L amber glass bottles at ambient conditions.

#### 2.1.1. MEROX fuels

Seven ambiently aged fuels were included from a refinery known to use a MEROX finishing process. These fuels have no requirement for antioxidant addition. The Aging 1 and Aging 2 samples were the same fuel with Aging 2 containing the military additive package. It was found that Aging 2 still contained 9.4 ppm of antioxidant even after 17 years in ambient storage, Table 1.

#### 2.1.2. Hydrotreated fuels

A range of ambient aged hydrotreated jet fuels, and a fresh 100% hydrotreated fuel with no antioxidant added was used as a reference standard. The reference hydroprocessed fuel, designated AO-24, was obtained from a local refiner and was 1 day old when received; this sample was subsequently stored at −18 °C. All of the F-44 samples were taken from a single location and known to be 100% hydrotreated, Table 3.

#### 2.1.3. Model fuel

The model fuel composition was chosen to examine storage stability of the alkane and aromatic fractions of fuel and did not contain any diaromatics as added to other model fuels compositions [21]. The model fuel used was as that of Webster et al. [22] and was made up of the following components;

a. 50 mL methyl cyclohexane.
b. 50 mL 2,2,4-trimethylpentane.
c. 100 mL toluene.
d. 100 mL *o*-xylene.
e. 100 mL nonane.
f. 50 mL decane.
g. 100 mL undecane.
h. 250 mL dodecane.
i. 200 mL tetradecane.

**Table 2**
MEROX and model fuel PetroOxy results.

| Sample | Years in ambient storage | PetroOxy time, min |
|---|---|---|
| Model fuel | 0 | 297 |
| Model fuel + 24 ppm AO | 0 | 1356 |
| Aging 6 – MEROX | 3 | 1715 |
| Jet A1 69% MEROX | 6 | 923 |
| Aging 5 – MEROX | 10 | 1760 |
| Aging 4 – MEROX | 11 | 1790 |
| Aging 3 – MEROX | 12 | 1417 |
| Aging 1 – MEROX | 17 | 974 |
| Aging 2 – MEROX | 17 | 1734 |

*Note* Aging 2 sample is Aging 1 that had the military additive packed added when produced.

**Table 3**
Ambiently aged hydrotreated fuels peroxide concentrations pre and post addition of antioxidant and measured after 13 weeks aging at 43 °C.

| Sample name | Fuel type | Years in ambient storage | PV initial (ppm) | PV 13 weeks at 43 °C with 25 ppm AO added | PV 26 weeks at 43 °C with 25 ppm AO added (ppm) | Initial AO present (ppm) | Sulfur concentration (ppm) |
|---|---|---|---|---|---|---|---|
| AO-24 | Jet A1 | 0.01 | 0.6 | | 15.7 | 0.0 | 11 |
| AO-10 | F-34 | 0.5 | 0 | | 12.2 | 14.2 | 85 |
| AO-34 | F-34 | 0.5 | 0.1 | 3.3 | | 13.1 | 297 |
| AO-35 | F-34 | 0.5 | 1.3 | 2.5 | | 16.9 | 304 |
| AO-18 | F-44 | 2 | 1.6 | | 13.1 | 6.5 | 9 |
| AO-11 | F-44 | 2 | 1 | | 14 | 8.8 | 10 |
| AO-05 | F-44 | 2 | 3 | | 15.9 | 10.2 | 95 |
| AO-14 | Jet A1 | 3 | 0.4 | | 7.2 | 2.3 | 185 |
| AO-06 | F-44 | 3 | 0 | | 15.4 | 0.0 | 14 |
| AO-33 | F-34 | 7 | 0 | 1.6 | | 13.7 | 19 |
| AO-19 | Jet A1 | 9 | 3.1 | | 9.7 | 13.5 | 9 |

### 2.2. Assessment of storage stability

Two methods were used to assess the stability of fuels storage stability, a modified ASTM D4625 Standard Test Method for Distillate Fuel Storage Stability at 43 °C with subsequent peroxide analysis and without analysis of insolubles, and ASTM D7545 Oxidation Stability of Middle Distillate Fuels-Rapid Small Scale Oxidation Test (RSSOT). Fuels were aged using ASTM D4625 which has been reported to correlate well with fuels in field storage [23]. Peroxide concentration of the fuel was tested before aging and prior to addition of antioxidant and then again after the addition of 25 ppm of 2,6-di-*tert*-butyl phenol and subsequent aging at 43 °C. Samples were tested at 13 or 26 weeks. Peroxide testing was performed using ASTM D3703 standard test method for hydroperoxide number of aviation turbine fuels, gasoline and diesel fuels applied to a Mettler Toledo T50 titrator (Mettler-Toledo International, Columbus, Switzerland).

Induction time testing was undertaken by ASTM D7545 using a PetroOxy instrument (PetroTest Instruments, Dahlewitz, Germany) which determines oxidation stability by heating 5.0 mL of fuel at 140 °C under an oxygen atmosphere at 700 kPa. The stability result is the time taken for a 10% drop in the oxygen pressure. The PetroOxy instrument is normally used for diesel fuels, however, when used for a range of jet fuels it has been found to have good repeatability for jet fuel induction period assessment at ±6%. This repeatability value was generated by running the three different fuel samples five times each. Sulfur contents were measured following a method based on gas chromatography–atomic emission detection [24].

### 2.3. GCMS analysis of antioxidants

Antioxidant concentrations were quantified using an Agilent 7890A-5975C GCMS (Agilent Technologies, Santa Clara, USA) operating in selected ion monitoring (SIM) mode and equipped with a split/splitless inlet and a HP-5 ms column (30 m × 0.25 mm I.D. and 0.25 μm). Automated sample preparation and injection was performed using an Agilent 7693 automatic liquid sampler; 8 μL of internal standard was dosed into 92 μL of sample and mixed at 3000 rpm for 13 s in a bidirectional mixing mode. 0.7 μL injections of sample were made with the autosampler.

The analytical conditions were based on GC–MS-SIM methods described by Bernabei et al. and Morris [25,26]. The measurements were carried out with a 50:1 split and an injection temperature of 250 °C. The oven temperature profile was as follows: an initial temperature of 60 °C, held for 1 min; then 8 °C/min to 130 °C and held for 3 min; 10 °C/min to 171 °C and held for 1 min; and 30 °C/min to 310 °C and held for 3 min. The total run time was 25.5 min. A solvent delay of 11 min was used. The carrier gas was helium and the average velocity was 29.6 cm/s.

The operating conditions of the mass selective detector (MSD) were as follows: the mass transfer line temperature was 280 °C, electron impact ionisation in positive mode (EI+) with 70 eV ionisation energy. The following ions were acquired in SIM mode to measure the concentration of the phenolic antioxidants:

| Standard | Ions, *m/z* |
|---|---|
| 2,6-di-*tert*-butyl-4-methylphenol | 205, 220 |
| 2-*tert*-butyl-4,6-dimethylphenol | 135, 163, 178 |
| 2,6-di-*tert*-butylphenol | 191, 206, 192 |
| 2,4,6-tri-*tert*-butylphenol | 161, 247, 262 |
| 2-fluorobiphenyl (internal standard) | 83, 141, 169 |

### 2.4. MDGC analysis of antioxidants

Heart-cut analyses were carried out on an Agilent 7890A GC with 5975C single quadrupole mass spectrometer (Agilent Technologies, Santa Clara, USA) equipped with a Deans switch assembly. The GC oven was programmed as follows; 60 °C for 1 min, 8 °C/min to 130 °C for 3 min, 10 °C/min to 168 °C for 10 min, then 30 °C/min to 250 °C for 5 min. The multimode inlet was operated in split mode at 50:1 and heated to 250 °C. Helium carrier gas was supplied at constant pressure of 39.51 psi to the primary column, and 26.27 psi to the Deans switch. Separations of 0.2 μL of sample were completed through a HP-5 ms (30 m × 0.25 mm × 0.25 μm) capillary column in the first dimension. The deactivated fused silica restrictor column was 0.64 m × 0.1 mm and the second dimension column was a BPX-90 (30 m × 0.25 mm × 0.25 μm). Mass spectral data were collected in scan/SIM mode, scanning over the range *m/z* = 50–350, and SIM on the ions specified in the previous section.

### 2.5. GCMS analysis of naphthalene, tetralin and decalin

GCMS was used to determine the concentration of naphthalene, tetralin and decalin in the samples. The experimental conditions were as per Section 2.3 using external calibration with tetralin as a standard. Results were calculated on selected ions for naphthalene, *m/z* 128, tetralin, *m/z* 104 and decalin *m/z* 138.

## 3. Results and discussion

All fuels were examined for initial antioxidant content and of the four antioxidants examined, only two were observed,

**Table 4**
Hydroprocessed fuels PetroOxy results with re-addition of antioxidant.

| Description of hydrotreated fuel | Age (years in ambient storage) | Sample | Antioxidant (ppm) | Sulfur (ppm) | PetroOxy (time in minutes to 10% loss of oxygen) |
|---|---|---|---|---|---|
| Jet A1 fresh refinery 100% HT no AO | 0 | AO-24 | 0.0 | 10.0 | 361 |
| F-44 | 2 | AO-32 | 13.5 | 3.7 | 346 |
| F-34 | 7 | AO-33 | 16.8 | 19.1 | 349 |
| F-34 | 1 | AO-34 | 13.1 | 296.0 | 294 |
| Jet A1 fresh refinery100% HT + 20 ppm BHT | 0 | AO-24-BHT | 20 | 10.0 | 437 |
| F-44 + 20 ppm BHT | 2 | AO-32 + BHT | 33.5 | 3.7 | 407 |
| F-34 + 20 ppm BHT | 7 | AO-33 + BHT | 36.8 | 19.1 | 397 |
| F-34 + 20 ppm BHT | 1 | AO-34 + BHT | 33.1 | 296.0 | 377 |
| F-44 + 100 ppm BHT | 2 | AO-32 + 100 BHT | 113.5 | 3.7 | 649 |
| F-34 + 100 ppm BHT | 7 | AO-33 + 100 BHT | 116.8 | 19.1 | 755 |
| F-34 + 100 ppm BHT | 1 | AO-34 + 100 BHT | 113.1 | 296.0 | 552 |
| F-44 HMAS Stirling | 2 | AO-18 | 6.5 | 9.2 | 320 |

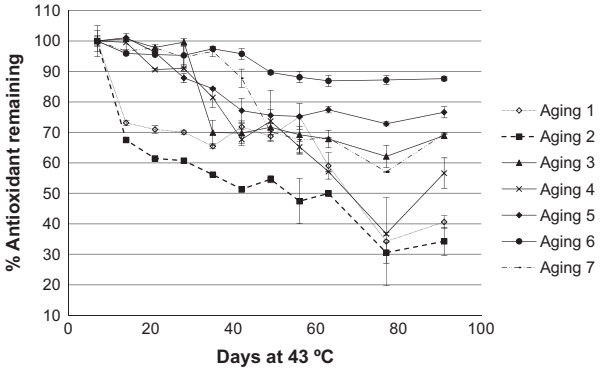


**Fig. 1.** Antioxidant depletion after re-addition for MEROX fuels. Samples Aging 2 and 3 contained residual antioxidant as per Table 1.

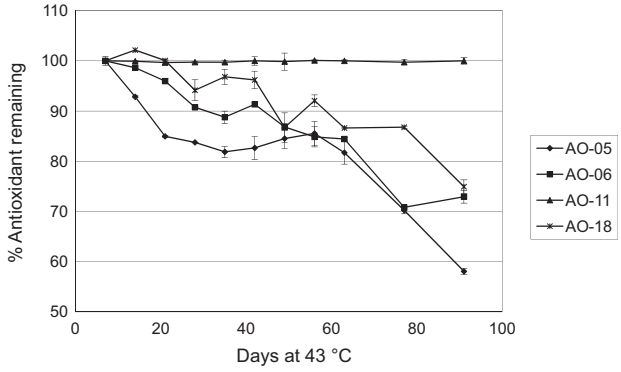


**Fig. 2.** Antioxidant depletion after re-addition for hydroprocessed F-44 fuels.

2,6-di-*tert*-butylphenol and 2,4,6-tri-*tert*-butylphenol. Re-addition of antioxidant to aged and fresh fuels was examined in three distinct groupings, MEROX, hydroprocessed and F-44. The F-44 samples were examined as a sub-set of the hydroprocessed samples as it was believed they had undergone more severe hydroprocessing.

### 3.1. MEROX

No peroxides were observed in any of the MEROX fuels prior to aging at 43 °C, as shown in Table 1. It is known that the presence of sulfur compounds can act to reduce peroxide formation by a decomposition process [27,28]. All but one MEROX fuel produced peroxides after 26 weeks storage at 43 °C. The Aging 7 fuel was approximately 6 months old and did not produce measurable peroxides. There was insufficient sample to track peroxide formation at regular time intervals for all of the samples.

The fuels were examined via the PetroOxy test without further addition of antioxidant, with the results in Table 2. There is no current limit set for rating of jet fuel stability by this method; however the long induction times observed for the MEROX fuels are all significantly greater than those for hydroprocessed fuels, Table 4. Thus the rate of oxygen consumption in stressed MEROX fuels is lower than that for hydroprocessed fuels. This result infers that the MEROX fuels still contain significant natural antioxidant capacity even after time in storage. The PetroOxy results for Aging 1 and 3 samples show that the antioxidant package after 17 years still provides longer induction times, and is more resistant to oxidation than the Aging 1 sample that does not have the military additive package.

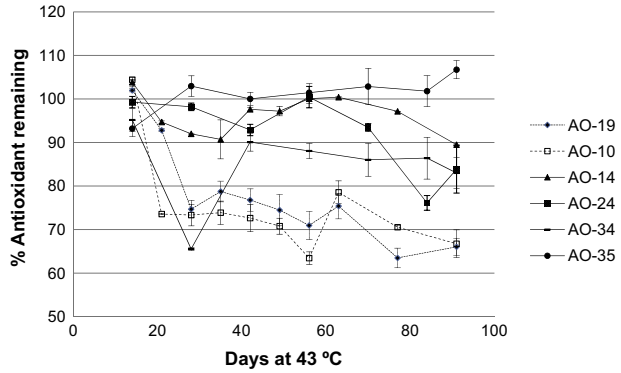


**Fig. 3.** Antioxidant depletion after re-addition for hydroprocessed F-34 and F-35 fuels.

The rate of depletion of the synthetic antioxidant was in general greater for MEROX fuels which suggests the synthetic antioxidant is consumed in preference to naturally occurring antioxidant species, Fig. 1. The addition of antioxidant to the aged MEROX fuels has not inhibited the formation of peroxides using 43 °C storage stressing conditions.

### 3.2. Hydroprocessed

The AO-24 sample represented a fresh refinery fuel known to have been 100% hydroprocessed and had no antioxidant added. It was found to contain peroxides after less than one week of storage post production. Of the ambiently aged fuels all but one contained residual antioxidant and many contained measurable quantities of peroxide.

After 26 weeks at 43 °C all fuels produced greater than 7 ppm peroxides which was the maximum allowable concentration of peroxides previously controlled by the USN JP-5 specification MIL-DTL-5624 [29]. Whilst this specification requirement has since been removed it gives an indication of the degree to which these fuels have oxidised to produce peroxides during storage at 43 °C, Table 3.

The rate of antioxidant depletion in re-additised F-34 and F-44 fuels was observed to be lower than that for the MEROX fuels Figs. 2 and 3, indicating that the re-addition of antioxidant did not inhibit formation of peroxides whilst not being consumed during the ageing process.

#### 3.2.1. Hydroprocessed PetroOxy

A sub-set of hydroprocessed fuels were examined using the PetroOxy method, Table 4. The fuels were tested after ambient storage then with addition of butylated hydroxytoluene (BHT) at two concentrations. All of the fuels were observed to have similar oxygen induction times and all showed improvement in resistance to oxidation after addition of BHT.

The rate of antioxidant depletion in re-additised fuel showed rates of almost no loss to just over 40% loss. This was a surprising result as hydroprocessed fuels are often considered to be fast oxidisers due to their lack of natural antioxidant species and their reliance on the synthetic phenolic antioxidant. The re-addition of antioxidant to these hydroprocessed fuels has in some cases stabilised the rate of loss of antioxidant and thus the potential for formation of gums and peroxides. The addition of antioxidant to the AO-24 freshly hydroprocessed sample showed that antioxidant was lost at a rate consistent with ambiently aged fuels.

### 3.3. Level of hydroprocessing

Due to fuel in storage facilities often being mixtures of fresh fuel from a known refinery or process, aircraft defuels from unknown sources and potentially fuels from unknown finishing process, for some samples it was difficult to be positive of its degree of hydroprocessing. It is well known that blending fuels can significantly alter stability aspects of the blend [30,31].

A method was examined to try to develop a laboratory technique for determining an unknown fuels degree of hydroprocessing. The method was related to its sulfur content and the concentration of specific hydroaromatic species in the fuel. Tetralin is a hydroaromatic compounds and along with decalin, while naturally occurring in fuel, may also be formed during hydroprocessing by reduction of naphthalene.

No direct correlation was observed between sulfur concentration and tetralin level. The ratio of tetralin to naphthalene was also examined to see if correlation could be made between the concentration of naphthalene and that potentially converted to tetralin during hydroprocessing. No correlation was observed. A stronger correlation was observed between sulfur and decalin concentration, Fig. 4. Note two of the fuels in the data set were out of the maximum specification limit of 3000 ppm.

Morris examined the effect of addition of antioxidant to aged fuels and observed antioxidant was rapidly consumed but was effective in stabilising peroxide formation. His work found that antioxidant would not remediate high hydroperoxide levels attained in a reactive fuel [25]. This work also concluded that very low concentrations of hydroperoxides formed in hydroprocessed fuels both with and without antioxidant addition and no obvious benefits for storage stability was found with the addition of antioxidant, however addition to antioxidant post aging did inhibit further formation of hydroperoxides.

### 3.4. Multidimensional GCMS

Due to the complexity of the chromatogram and some abnormal changes in the measured antioxidant concentrations, the region in which the antioxidants eluted was examined by multidimensional gas chromatographic techniques. A heart-cut of the antioxidant region was sent to a second column to assist in deconvolving the complex chromatogram.

The heart cutting approach clearly demonstrates the difficulties encountered in quantifying antioxidant compounds even using high resolution GC separations. Despite the heart cut transferral of the small antioxidant elution region to a second dimension space, there are still interferences from other fuel components,

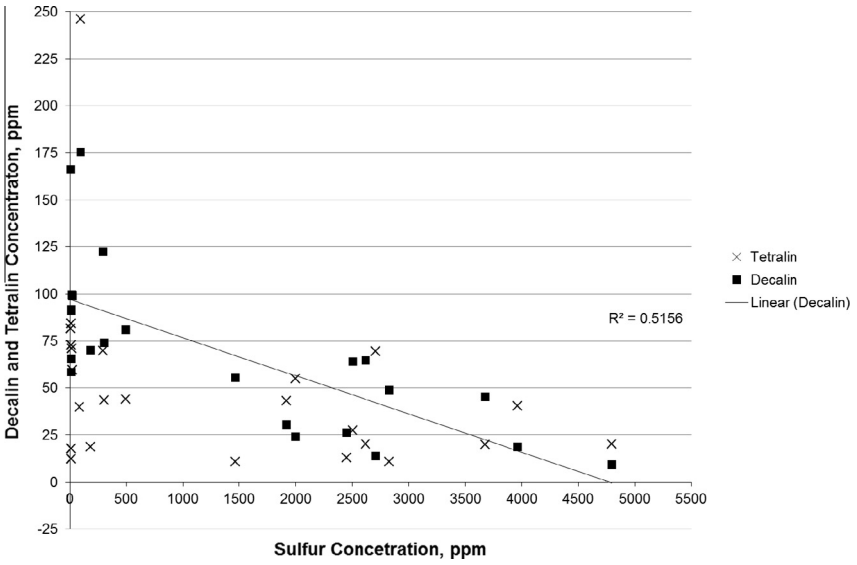


**Fig. 4.** Correlation of decalin and tetralin concentration with sulfur content.

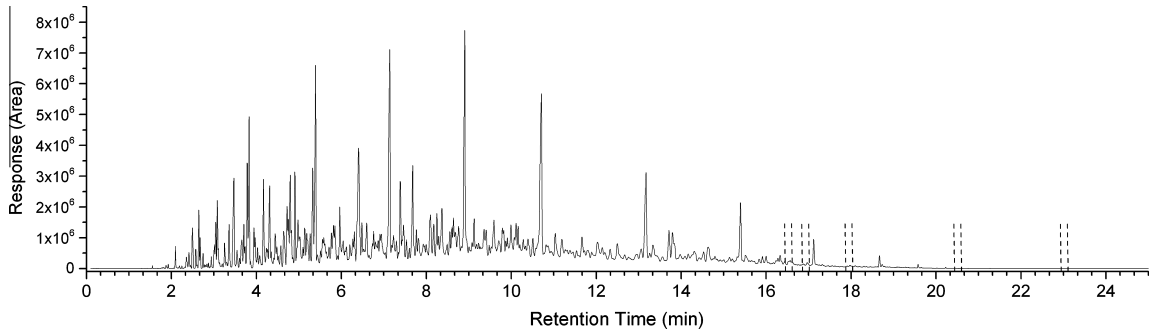


**Fig. 5a.** First dimension chromatogram of MEROX fuel. Vertical dashed lines indicate heart cut regions corresponding with the retention time of antioxidants.

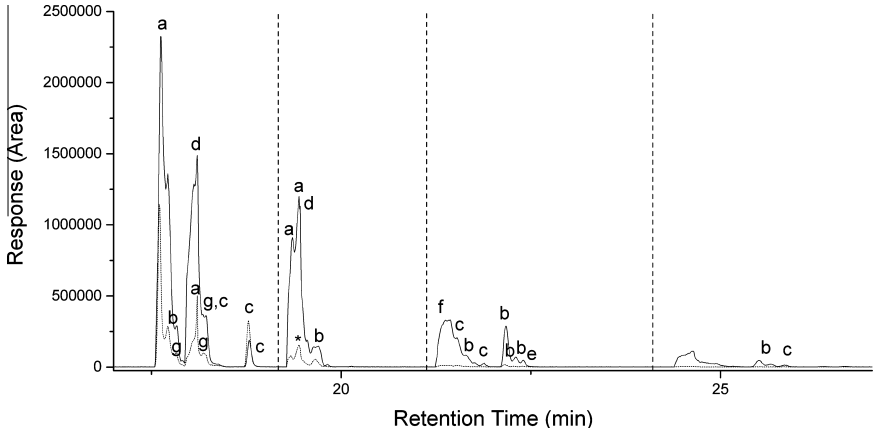


**Fig. 5b.** Heart cut chromatogram of a MEROX (solid line) and hydrotreated (dotted line) fuel. Vertical dashed lines indicate elution space of four separate heart cut regions. Letters above peaks indicate the class of compound identified; (a) normal or branched alkane, (b) alkyl naphthalene or hydroaromatic, (c) biphenyls, (d) alkyl cycloalkanes, (e) alkyl azulene, (f) alkyl alcohol and (g) alkyl benzenes. Asterisk indicates an antioxidant compound.

and baseline resolution of the compounds of interest is rarely achieved. There is little advantage to be gained by exploiting the polarity of synthetic antioxidant additives, particularly in MEROX or fuels which have been only slightly hydroprocessed and still retain a significant portion of polyaromatic and other polar species that coelute with the compounds of interest under the conditions explored in this study (see Figs. 5a and 5b).

## 4. Conclusion

The re-addition of antioxidant to a range of MEROX and hydroprocessed fuels subsequently aged at 43 °C was found in general to have little effect on the formation of peroxides. There is little benefit in adding a synthetic antioxidant to a MEROX fuel as they are sufficiently stable as produced. Hydroprocessed fuels all produced measurable peroxides after storage for 13 and 26 weeks at 43 °C, while still having remaining antioxidant, indicating the antioxidant is not effective in inhibiting peroxide formation under these conditions. Stability performance based on oxygen induction times showed that all fuels were improved with re-addition of antioxidant. An unknown fuel's level of hydroprocessing may be best estimated by comparison of its sulfur and decalin contents.

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